#### **APPENDIX**

# **Underway CO<sub>2</sub> Measurements aboard the RVIB Palmer and Data Management of the Global VOS Program**

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#### 1. SCIENTIFIC OBJECTIVES

The sea-air net flux of CO<sub>2</sub> is governed by the difference between pCO<sub>2</sub> in surface ocean water and the overlying atmosphere as well as by the gas transfer rate across the sea-air interface. The former depends primarily on the processes occurring within the sea (such as seawater temperature, biological productivity and upwelling of deep waters), and the latter is controlled mainly by turbulence in the interface zone induced by winds. The primary objective of this proposed investigation is to determine the space-time distribution of the sea-air pCO<sub>2</sub> difference. In conjunction with CO<sub>2</sub> gas transfer coefficients which are being improved by other scientific groups, a reliable net sea-air flux of CO<sub>2</sub> estimate over regional to global scales can be obtained using improved sea-air pCO<sub>2</sub> difference data.

#### 2. THE LDEO PROGRAM

## 2.1. Field Program:

The field work by the LDEO group is primarily focused in the southern high latitude ocean areas surrounding the Antarctic continent. The LDEO group operates a semi-automated surface water pCO<sub>2</sub> system aboard the RVIB Nathaniel Palmer with significant operational assistance from the Raytheon Polar Support group (funded by NSF). RVIB Palmer is an ice-breaking research vessel, one of the few research ships operated, even during winter months, in the high latitude Southern Ocean areas including the Weddell and Ross Seas and the formation areas for the deep and intermediate water masses. Hence, this program yields observations critical to our understanding of the role of the Southern Ocean in the global carbon cycle (see Figure 1). Our Southern Ocean study is further strengthened by the cooperation with the NSF's Drake Passage CO<sub>2</sub> program aboard the R/V Laurence M. Gould, that is conducted jointly with Colm Sweeney of ESRL/NOAA and the LDEO group.

In order to document time-space distribution of surface water pCO<sub>2</sub> in the Arctic, we have initiated a program with U. S. Coast Guard and NSF for a long-term operation of our pCO<sub>2</sub> system aboard USCGC Healy, which is operated primarily in the Arctic Ocean. Our proposed program has been approved by the Arctic Icebreaker Coordinating Committee (consisting of the representatives of USCG, NSF and researchers), and is in progress (see Section 3.2.).

## 2.2. Data Management Program

Under this grant, the Lamont-Doherty Observatory group is responsible for qualitycontrol and management of the data produced by the NOAA-supported groups as well as those from international collaborators from Japan, Iceland, Germany, UK and France. Pooling of the data from these participants allows us to cover a large part of the global oceans. During this grant period, a global ocean database which includes 4.1 million surface ocean pCO<sub>2</sub> observations made in 1970 through the end of 2007 has been assembled in a single uniform format (LDEO Database, version 2007) and is accessible to the public through the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge National Laboratory. TN (Takahashi et al.. 2008 http://cdiac.ornl.gov/oceans/LDEO Underway Database/LDEO home.html). This is an updated and improved version of the earlier release (version 1.0), which contains about 3.4 million pCO<sub>2</sub> measurements. The detailed data in current years are also accessible to the VOS participants via the LDEO web site (www.ldeo.columbia.edu/CO2).

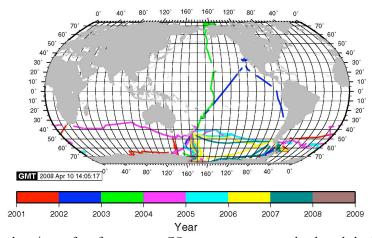
### 3. PROGRESS TO DATE, LDEO Program

The progress made during the current funding period September, 2007 through August, 2008, is described in this section.

#### 3.1. LDEO Field Program aboard the RVIB Palmer

The Lamont group is primarily responsible for the acquisition of the surface water pCO<sub>2</sub> data aboard the RVIB Palmer. The ship was not at sea during the period May 10 through August 27, 2007, for refit in a dry dock and test cruises, and no data were obtained. On September 1, 2007, our measurement program was resumed. During the expeditions, we obtained the following information: pCO<sub>2</sub> in surface ocean water, SST, salinity, wind speeds, barometric pressure and atmospheric CO<sub>2</sub> concentration. The data were obtained successfully for better than 98% of time during the at-sea periods.

The locations of our data obtained since the beginning of this project in 2001 are shown in Figure 1, and the dates, location and number of measurements are listed in Table 1. The total number of surface water pCO<sub>2</sub> data obtained to date is 668,537, of which 76,112 measurements were added to the database during this project year, September, 2007 through August, 2008.



**Figure 1.** The locations of surface water  $pCO_2$  measurements made aboard the RVIB Palmer since 2001. During the current project year August, 2007-August, 2008 (dark green and brown lines), about 76,112  $pCO_2$  measurements were obtained.

**Table 1.** List of the RVIB N. B. Palmer expeditions and the number of surface water pCO<sub>2</sub> measurements obtained from January, 2001 through August, 2008.

	m January, 2001 unough August, 2006.			
Cruise No	. Project Name	Dates	No. Obs.	Annual No.
01/1	East Antarctic Margin	30 Jan - 20 Mar 2001	12,300	
01/2	SouthWest Pacific	01-19 Apr 2001	6,541	
01/3	SO-GLOBEC	23 Apr - 06 Jun 2001	20,446	
01/4	SO-GLOBEC	21 Jul - 01 Sep 2001	14,960	
01/5	Antarctic Peninsula	07 Sep - 26 Oct 2001	27,312	
01/6	SO-GLOBEC	09 Nov- 01 Dec 2001	10,317	
01/7	Antarctic Peninsula	05 Dec 01 - 12 Jan 02	22,627	114,503
02/1	Antarctic Penninsula	18 Jan - 04 Mar 02	24,542	
02/2	GLOBEC III	09 Apr - 21 May 2002	25,327	
02/4	GLOBEC IV	31 Jul - 09 Sep 2002	29,640	
02/5	Transit along W. South America	23 Sep - 19 Oct 2002	8,317	
02/6	USCG Inspection	30 Oct - 08 Nov 2002	6,732	
02/7	Reconst. of Paleo S. Pac.	10 Nov - 06 Dec 2002	5,702	
02/9	ANSLOPE, Transit fm Lyttleton to McMurdo	11 Dec 2002 - 03 Jan 2003	6,925	107,185
03/1	Ross Ice Shelf Survey	5 - 30 Jan 2003	8,062	
03/1A	Ross Sea Research	2-20 Feb 2003	7,227	
03/2	Ross Sea Research	25 Feb - 09 Apr 2003	13,897	
03/4	Transit N.Z to Alaska	23 May - 02 Jul 2003	9,864	
03/4A	Alaska North Slope	06 Jul - 18 Aug 2003	17,136	
03/5	Southern Ocean near 175E	26 Oct - 13 Dec 2003	7,427	
03/5A	Ross Sea Research	18 Dec 2003 - 02 Jan 2004	4,501	68,114
04/1	Western Ross Sea	20 Jan - 19 Feb 2004	12,299	
04/2	ANSLOPE III	26 Feb - 11 Apr 2004	17,708	
04/3	Transit New Zealand to Chile	16 Apr - 12 May 2004	9,463	
04/4	Ice Fish	18 May - 19 Jul 2004	22,755	
04/6	Transit, South Africa to New Zealand	27 Jul - 04 Sep 2004	14,277	
04/8	ANSLOPE IV	12 Oct - 06 Dec 2004	21,958	

04/9	Biochemical Research	18 Dec 2004 - 25 Jan 2005	14,443	112,903
05/1	ANSLOPE/IVARS	28 Jan - 15 Feb 2005	5,736	
05/1B	N.Z. to Chile Transit	03 - 22 Mar 2005	7,494	
05/2	Antarctic Penninsula	02 - 24 Apr 2005	8,235	
05/5	Coastal Chile	23 Jun - 14 Jul 2005	3,983	
05/6	Maud Rise	20 Jul - 18 Sep 2005	19,066	
05/7	Chile to N.Z. Transit	23 Sep - 21 Oct 2005	9,554	
05/8	Ross Sea Biology	26 Oct - 12 Dec 2005	18,387	72,455
06/1	Interaction of Iron, Light, & CO2	17 Dec 05 - 30 Jan 06	16,174	
06/2	Late Cretaceous & Cenozoic Recreations	03 Feb - 23 Mar 2006	7,740	
06/3	Paleo History of Larsen Ice Shelf	12 Apr - 05 May 2006	10,005	
06/6	Plankton Community Struct & Iron Concent.	03 Jul - 18 Aug 2006	17,565	
06/8	Ross Sea Plankton Dynamics	01 Nov - 15 Dec 2006	17,257	68,741
07/1	Geological Research	22 Dec 2006 - 29 Jan 2007	14,963	
07/2	Amundsen Sea Research	03 Feb - 25 Mar 2007	20,780	
07/3	Collaborative Research	31 Mar - 05 May 207	12,781	
07/4	Open Period	10 May - 20 Jun 2007	no data	
07/5	Transit to Maintenance Period	21 - 25 Jun 2007	no data	
07/6	Dry dock	25 Jun - 28 Jul 2007	no data	
07/7	Transit to Punta Arenas, Chile	28 Jul - 02 Aug 2007	no data	
07/8	Open Period	02 - 27 Aug 2007	no data	
07/9	Sea Ice Balance in the Antarctic	01 Sep - 31 Oct 2007	14,616	
07/10	Palmer Station Resupply	14 Nov - 07 Dec 2007	8,548	
07/11	Transit, Chile - New Zealand	14 - 30 Dec 2007	6,355	78,043
08/1	Ross Sea Research	08 - 27 Jan 2008	6,876	
08/2	Ross Sea Research	29 Jan - 20 Feb 2008	8,562	
08/3	Ross Sea Research	23 Feb - 17 Mar 2008	8,330	
08/4	Transit, New Zealand to Chile	21 Mar - 14 Apr 2008	9,300	
08/5	Drake Passage, Scotia Sea Research	18 Apr - 25 May 2008	13,525	
08/6	Weddell Sea	31 May - 30 Jun 2008	pending	
08/7	Not Used			
08/8	Drake Passage	Pending	pending	46,593

#### **GRAND TOTAL SINCE THE BEGINNING OF THE PROJECT**

668,537

## 3.2. LDEO Field Program aboard the R/V Marcus Langseth and USCGC Healy

We are working toward adding our underway pCO<sub>2</sub> systems on two ships. R/V Marcus Langseth, which is newly acquired by the Lamont-Doherty Earth Observatory with support from NSF, has undergone the first sea trial in March, 2008, and an underway pCO<sub>2</sub> system has been installed on board in May, 2008. However, its underway pumping system for scientific water samples has been found to be unreliable and problematic. For this reason, no reliable pCO<sub>2</sub> data have been obtained through the end of September, 2008, the terminal day for the NSF's ship operation funding for 2008. Our pCO<sub>2</sub> program will resume when the ship will be put to the sea in 2009.

A pCO<sub>2</sub> system for USGCC Healy has been completed ahead of the schedule and is ready for the installation as soon as a new, improved underway pumping system for scientific purposes (funded by NSF) is completed aboard the ship. However, it appears that the completion of the pumping system may be delayed until the later half of 2009. As soon as the pumping system is completed, our measurement program in the Arctic Ocean will be started.

## 3.3. pCO<sub>2</sub> Data Processing and Management at LDEO for the VOS Program

Under this grant, the Lamont-Doherty Observatory group is responsible for quality-control and management of the data produced by the NOAA-supported Volunteer Ocean Survey (VOS) groups as well as those from international collaborators from Japan, Iceland, Germany, UK and France. A global ocean database which includes 4.1 million surface ocean pCO<sub>2</sub> observations made in 1970 - 2007 has been assembled in a single uniform format (LDEO Database, version 2007, Takahashi et al., 2008) and is accessible to the public through the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge

National

Laboratory,

TN

(<a href="http://cdiac.ornl.gov/oceans/LDEO\_Underway\_Database/LDEO\_home.html">http://cdiac.ornl.gov/oceans/LDEO\_Underway\_Database/LDEO\_home.html</a>). This is an updated and improved version of the earlier release (version 1.0), which contained about 3.4 million pCO<sub>2</sub> measurements.

For the members of the (VOS) consortium, the participants are able to access the data in a uniform electronic format. For this purpose, we have established an open web site at the following URL: <a href="http://www.ldeo.columbia.edu/CO2">http://www.ldeo.columbia.edu/CO2</a>. The site provides not only the numerical data, but also maps showing the ship's tracks for each data file. The new data will be accessible only to the VOS participants for a period of three years, and will be released to the public after this period. The field data from the following field operations constitute major additions to the database; 1) the RVIB Palmer program in the Southern Ocean; 2) the R/V Laurence M. Gould program, which is supported by NSF as a part of the Long-Term Research in Environmental Biology (LTRE) program in the Drake Passage-Antarctic Peninsula area, Southern Ocean; 3) the "Explorer of the Seas" program in and around the Caribbean Sea (R. Wanninkhof); 4) the Kaimimoana program in the equatorial Pacific (R. A. Feely); 5) the Container Ship Oleander and Atlantic Explorer programs (N. Bates, BIOS) in the temperate western North Atlantic); and 6) the M/V Turmoil program for coastal waters (T. Takahashi).

The number of surface water pCO<sub>2</sub> observations reported to us for incorporation into our database is summarized in Table 2. During this funding period, 332,845 pCO<sub>2</sub> data accompanied with SST, salinity and other information have been added to the database.

<b>Table 2.</b> Summary of the new	data contributed to the database by the	he VOS participants during this funding
period, August, 2007 – August	, 2008.	

Programs	PI / Institutions	No. of pCO <sub>2</sub>	Primary
		<b>Observations</b>	Locations
RVIB Palmer	Takahashi/LDEO	76,112	Southern Ocean
R/V Gould	Sweeney/ESRL/NOAA	68,403	Drake Passage,
	Takahashi/LDEO		Southern Ocean
Explorer of Seas	Wanninkhof/AOML/NOAA	53,268	Caribbean
R/V Kaimimoana	Feely/PMEL/NOAA	57,721	Tropical Pacific
M/V Oleander	Bates/BOIS	Not reported	N. Atlantic
R/V Atlantic Explorer	Bates/BIOS	Not reported	Bermuda
M/V Turmoil	Takahashi/LDEO	101,053	Coastal
TOTAL FOR			
AUG. 07-AUG. 08		356,557	

#### 3.4. LDEO Data Analysis and Synthesis

The pCO<sub>2</sub> data obtained and archived by the present grant have been used extensively in the following research papers and government reports, that have been prepared during this grant period, 2007-08.

Takahashi, T., Sutherland, S. C. and Kozyr, A., 2008: Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database: Measurements Performed during 1968-2006 (Version 1.0). ORNL/CDIAC-152, NDP-088. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, TN 37831, pp.20. (With 3.4 million pCO<sub>2</sub> measurements in global surface ocean waters.)

Takahashi, T., Sutherland, S. C. and Kozyr, A., 2008: Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database: Measurements Performed during 1968-2007 (Version 2007). ORNL/CDIAC-152, NDP-088. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, TN 37831, pp.20. (With 4.1 million pCO<sub>2</sub> measurements in global surface ocean waters.)

Takahashi, T. S.C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, C. Sabine, J. Olafsson, Th. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, Richard Bellerby, A. Körtzinger, T. Steinhoff, M. Hoppema, H. J. W. de Baar, C. S. Wong, Bruno Delille and N. R. Bates: Climatological mean and decadal changes in surface ocean pCO<sub>2</sub>, and net sea-air CO<sub>2</sub> flux over the global oceans. *Deep-Sea Res. II*, in press.

S. C. Doney, I. Lima, J. K. Moore, K. Lindsay, M. Behrenfeld, N. Mahowald, M. Maltrud, D. M. Glover, D. McGillicuddy, and T. Takahashi: Skill metrics for confronting global upper ocean ecosystem-biogeochemistry models against field and remote sensing data. Jour. *Marine Systems*, Special Issue "Skill Assessment for Coupled Biological/Physical Models of Marine Systems" (Available on line, May 29, 2008), in press.

Sabine, C. L., Feely, R. A., Wanninkhof, R. and Takahashi, T.: The global ocean carbon

cycle. Bulletin of the American Meteorological Society, in review.

#### 3.5. Public presentations

Taro Takahashi, Rik Wanninkhof, Colm Sweeney, Richard A. Feely, Burke Hales, Jon Olafsson and Stewart C. Sutherland, 2007: Decadal change and climatological mean surface ocean pCO<sub>2</sub>, and net sea-air CO<sub>2</sub> flux over the global oceans. Invited presentation at the Gordon Research Conference, July, 2007, Meriden, NH.

Taro Takahashi et al., 2007: Climatological mean and decadal change in surface ocean pCO<sub>2</sub>, and net sea-air CO<sub>2</sub> flux over the global oceans. A key note address at the 16<sup>th</sup> meeting of the North Pacific Marine Science Organization (PICES), October, 2007, Victoria, CANADA.

Jon Olafsson, Taro Takahashi, Thorarinn.S. Arnarson, Solveig.R. Olafsdottir and Magnus Danielsen, 2008: Time series observations, 1983-2006, of inorganic carbon and nutrients in high latitude North Atlantic. ASLO-Ocean Sciences meeting, March, 2008, Orlando, FL.

Corinne Le Quere, Taro Takahashi, Christian Rödenbeck, Erik T. Buitenhuis, Steward C. Sutherland, 2008: Recent trend in the global oceanic CO<sub>2</sub> sink. International Symposium on the Effects of Climate Change on the World Oceans, May, 2008, Gijon, Spain.

L. Barbero-Munoz, J. Boutin, L. Merlivat, J. B. Sallee, T. Takahashi and S. C. Sutherland, 2008: Sea surface pCO2 in the subantarctic zone of the Southern Ocean from CARIOCA buoys and ship data. International Symposium on the Effects of Climate Change on the World's Oceans, May 19 - 23, 2008, Gijon, Spain.

#### 4. HIGHLIGHT OF THE LDEO PROGRAM

An extensive database for the surface water pCO<sub>2</sub> over the global oceans has been released through the Carbon Dioxide Information Center (CDIAC) to the public. This database contains about 4.1 million surface ocean water pCO<sub>2</sub> data accompanied with associated information such as the dates and positions of measurements, sea surface temperature, salinity and barometric pressures. This is an updated version of the earlier release (version 1.0) which contains about 3.4 million pCO<sub>2</sub> data.

A synthesis of the global surface ocean pCO<sub>2</sub> data has been accepted for publication in the SOCOVV Symposium volume of "Deep-Sea Research" (Takahashi et al., Deep-Sea Research, in press). The ocean uptake of  $CO_2$  is estimated to be about  $1.6 \pm 0.9$  Pg-C for the year 2000.